Anoxia in the terrestrial environment during the Late Mesoproterozoic

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ABSTRACT

A significant body of evidence suggests that the marine environment remained largely anoxic throughout most of the Precambrian. In contrast, the oxygenation history of terrestrial aquatic environments has received little attention, despite the significance of such settings for early eukaryote evolution. To address this, we provide here a geochemical and isotopic assessment of sediments from the Late Mesoproterozoic Nonesuch Formation of central North America. We utilize rhenium-osmium (Re-Os) geochronology to yield a depositional age of 1078 ± 24 Ma, while Os isotope compositions support existing evidence for a lacustrine setting. Fe-S-C systematics suggest that the Nonesuch Formation was deposited from an anoxic Fe-rich (ferruginous) water column. Thus, similar to the marine realm, anoxia persisted in terrestrial aquatic environments in the mid-late Proterozoic, but sulfidic water column conditions were not ubiquitous. Our data suggest that oxygenation of the terrestrial realm was not pervasive at this time and may not have preceded oxygenation of the

marine environment, signifying a major requirement for further investigation of links between the oxygenation state of terrestrial aquatic environments and eukaryote evolution.

Keywords: oxygenation; Precambrian; terrestrial environment; Re-Os; Fe speciation

INTRODUCTION

Recent reconstructions suggest that the global ocean remained anoxic between Earth's two major periods of rising atmospheric oxygen at either end of the Proterozoic Eon (2500 – 542 Ma). In detail, sulfidic water column conditions were prevalent along productive continental margins, overlying deeper waters that contained dissolved Fe (ferruginous) (Canfield et al., 2008; Poulton et al., 2010; Poulton and Canfield, 2011; Planavsky et al., 2011). However, in contrast to these advances in our understanding of the evolution of mid-Proterozoic ocean chemistry, much less is known about oxygenation of terrestrial aquatic environments during this period.

Recently, the determination of sulfur isotope fractionations between sulfate and sulfide ($\Delta^{34}S$) of >50‰ in lacustrine sediments from the Mesoproterozoic Torridon and Stoer Groups of NW Scotland, were interpreted to suggest that oxygenation of terrestrial aquatic environments preceded oxygenation of the oceans (Parnell et al., 2010). Such fractionations are generally considered to require an active oxidative sulfur cycle driven by disproportionation reactions involving sulfide-oxidising bacteria, and are interpreted to reflect a major rise in oxygen in the late Neoproterozoic (Canfield and Teske, 1996). If correct, this suggests that, unlike the marine realm, the late Mesoproterozoic terrestrial environment was sufficiently oxidized to support a complex biota adapted to an oxygen-rich atmosphere (Parnell et al., 2010). However, $\Delta^{34}S$ fractionations of 60-70‰ have recently been measured in an anoxic, low sulfate lake in the absence of oxidative sulfur cycling (Canfield et al.,

2010). This builds upon theoretical calculations of the magnitude of fractionation possible by bacterial sulfate reduction alone (Brunner and Bernasconi, 2005), and is supported by direct measurements of fractionations obtained during growth of a pure culture of bacterial sulfate reducers (Sim et al., 2011).

Considering the evolutionary significance of possible early oxygenation of terrestrial environments, coupled with these recent developments in our understanding of sulfur isotope fractionation, a more direct assessment of the redox state of the terrestrial realm during the late Mesoproterozoic is clearly warranted. Our focus is on the Nonesuch Formation, deposited within the ~1100 Ma intracratonic Mid-Continent Rift System of central North America (Ojakangas et al., 2001). Like the Torridon Group of NW Scotland, the Nonesuch Formation contains a rich record of eukaryotic life (Pratt et al., 1991; Strother and Wellman, 2010) and thus represents an ideal locality to assess possible links to early terrestrial oxygenation. We utilize Fe-S-C systematics to assess water column redox conditions, coupled with Re-Os geochronology to provide a depositional age for the Nonesuch Formation, and Os isotope systematics to yield insight into the nature of the depositional setting.

GEOLOGICAL SETTING

The Mid-Continent Rift System of central North America was one of the world's largest continental rifts (Ojakangas et al., 2001). In the Lake Superior region, up to 30 km of volcanic and sedimentary rift-fill sequences make up the Keweenawan Supergroup (Ojakangas et al., 2001; Fig. 1). The Oronto Group consists of fluvial and alluvial volcaniclastics, with the exception of the Nonesuch Formation, a 40 to 200 m thick succession of organic-rich siliciclastics. Geochronology of the Keweenawan Supergroup is based upon U-Pb zircon ages of rift-related volcanics, with the overlying post-rift sediments

poorly constrained temporally. An existing U-Pb zircon age of 1087.2 ± 1.6 Ma from the final andesite flow in the Copper Harbour Conglomerate (Davis and Paces, 1990; Fig. 1) provides a maximum age for the Nonesuch Formation.

To allow redox assessment using Fe-S-C systematics we have sampled well-preserved drillcore (PI-1) across a 60 m interval that covers the entire Nonesuch Formation (Pratt et al., 1991). These samples are augmented by Re-Os geochronology and Os isotope analyses of outcrop samples collected ~30 m above the Copper Harbour Conglomerate (Fig. 1; full details of the sampling and analytical protocols are provided in the GSA Data Repository). The Re-Os age for all the outcrop samples is 1040 ± 78 Ma (2σ, n = 16, Mean Squared of Weighted Deviation [MSWD] = 10.6; Fig. DR1; Table DR1). The large MSWD and uncertainty on this Re-Os date is due to variation in the initial $^{187}Os/^{188}Os$ (Os_i) values rather than disturbance to the isotope system, as suggested by the isochronous nature of the samples and agreement with the underlying U-Pb date (see GSA Data Repository). In fact, the Os_i values form two distinct groups, with eleven of the 16 samples yielding the most precise depositional age of 1078 ± 24 Ma (2σ, n = 11, MSWD = 1.05; Fig. DR1).

DEPOSITIONAL ENVIRONMENT

Sedimentological characteristics of the Nonesuch Formation and proximity to continental red-beds (Fig. 1), coupled with paleogeographic reconstructions suggesting that the nearest coastline was ~800 km away, indicating that the Nonesuch Formation was likely deposited in a lacustrine environment (Elmore et al., 1989; Imbus et al., 1992; Ojakangas et al., 2001). However, a marine embayment or estuarine environment has also been suggested based on the presence of specific biomarkers and S/C ratios (Pratt et al., 1991; Hieshima and Pratt, 1991). Biomarkers extracted from the Nonesuch Formation include low levels of 24-*n*-propylcholestane (Pratt et al., 1991), which is commonly, but not uniquely, found in rocks of

marine origin (Moldowan et al., 1990) and may in fact relate to the presence of eukaryotic organisms in the Nonesuch Formation. Thus, the presence of 24-*n*-propylcholestane at low concentration does not unambiguously denote a marine depositional setting for the Nonesuch Formation.

Enrichments in S/C ratios have previously been interpreted to reflect deposition of the Nonesuch Formation under sulfate-rich marine conditions (Fig. DR2; Hieshima and Pratt, 1991; Imbus et al., 1992). However, enhanced fixation of sulfide as a result of the absence of bioturbation in the Precambrian and (potentially) non-Fe limited conditions during ferruginous deposition, combined with differences in the metabolisability of Precambrian organic matter, could readily lead to the observed enrichments in sulfur and decoupling between sulfur and carbon under lacustrine conditions (e.g., Raiswell and Canfield, 2012).

Application of Re-Os geochronology provides an additional, novel constraint on the nature of the depositional environment by yielding the Os_i composition of the water column at the time of deposition, which can be used to distinguish between lacustrine and marine settings (Poirier and Hillaire-Marcel, 2011; Cumming et al., 2012). The Os_i derived from the Re-Os isochrons are 0.81 ± 0.28 and 0.49 ± 0.13 (Fig. DR1), which shows variations reflecting a balance between weathering of radiogenic Archean-Proterozoic cratonic lithosphere (~1.01; upper continental crust calculated at 1100 Ma; Esser and Turekian, 1993) and unradiogenic rift-related flood basalts (~0.13; Allegre et al., 1999). At 1100 Ma, seawater $^{187}Os/^{188}Os$ was relatively unradiogenic at ~0.3 (a value derived from two separate margins; Rooney et al., 2010; Azmy et al., 2008), and therefore the more radiogenic values measured for the Nonesuch Formation (0.81 and 0.49) suggest that minimal Os was sourced from the marine realm. Thus, the Os isotope data support sedimentological and paleogeographic evidence for lacustrine depositional conditions.

REDOX CONDITIONS

Water column redox conditions during deposition of the Nonesuch Formation were evaluated using Fe speciation. A biogeochemically 'highly reactive' Fe pool (Fe_{HR}) is analysed through a series of extractions (Poulton and Canfield, 2005). Modern and ancient sediments deposited under anoxic conditions commonly have Fe_{HR}/total Fe (Fe_T) ratios >0.38, in contrast to oxic depositional conditions, where ratios are consistently below 0.22 (Poulton and Canfield, 2011). About 40% of drill core samples (Fig. 2), and all outcrop samples (Table DR2), were clearly deposited from an anoxic water column with Fe_{HR}/Fe_T >0.38, while others fall within the equivocal range (Fe_{HR}/Fe_T = 0.22-0.38). These equivocal samples may reflect the masking of water column Fe_{HR} enrichments due to rapid sedimentation or transformation of non-sulfidized Fe_{HR} to clay minerals during burial diagenesis or metamorphism (Poulton and Raiswell, 2002; Poulton et al., 2010). The latter possibility can be evaluated by considering Fe/Al ratios (Fig. 2), whereby significant enrichments in Fe relative to both average shale (Lyons and Severmann, 2006) and typical oxic lacustrine sediments (e.g., Kemp and Thomas, 1976; Fagel et al., 2005) throughout the Nonesuch Formation provide strong evidence for anoxic depositional conditions. Post-depositional loss of Fe_{HR} can also be assessed through an extraction that targets Fe associated with clay minerals (termed poorly reactive silicate Fe; Fe_{PRS}) (Poulton et al., 2010). Extreme enrichment in Fe_{PRS} in the Nonesuch Formation (Fe_{PRS}/Fe_T values are well above the modern and Phanerozoic averages; Fig. 2; Poulton and Raiswell, 2002) suggests that significant loss of Fe_{HR} through authigenic clay mineral formation was responsible for reducing original depositional Fe_{HR}/Fe_T ratios (Poulton et al., 2010), supporting anoxic deposition for all Nonesuch Formation samples.

For samples showing evidence of anoxic deposition, the extent to which the Fe_{HR} pool has been pyritized (Fe_{py}/Fe_{HR}) can then distinguish euxinic (Fe_{py}/Fe_{HR} >0.7-0.8) from

ferruginous (Fe_{py}/Fe_{HR} <0.7-0.8) depositional conditions (Poulton and Canfield, 2011). All of the Nonesuch Formation samples have Fe_{Py}/Fe_{HR} ratios well below the euxinic threshold (Fig. 2), indicating anoxic ferruginous depositional conditions throughout and thus refuting the suggestion of a possible euxinic depositional setting (c.f. Imbus et al., 1992).

IMPLICATIONS FOR TERRESTRIAL BIOSPHERIC OXYGENATION

The upper Nonesuch Formation comprises fining and coarsening upward packages interpreted to be the transition between lacustrine deposition and fluvial conditions of the conformably overlying Freda Sandstone (Elmore et al., 1989). This suggests that the Nonesuch Formation was likely deposited under progressively more oxic conditions as water depth decreased towards the top of the succession (Elmore et al., 1989). Oxygenated surface waters in ~1.1 Ga terrestrial aquatic environments would be expected, particularly since shallow marine waters were apparently oxygenated much earlier in Earth history (~2.7 Ga; Kendall et al., 2010; Zerkle et al., 2012). However, we find no evidence for oxic deposition in core PI-1, suggesting that anoxia was a persistent feature throughout the depositional period, and any oxygenation was likely restricted to surface waters.

The observation of persistent ferruginous water column conditions suggests that the flux of Fe_{HR} to the lake overwhelmed the flux of sulfate (Poulton and Canfield, 2011). We note here that our Os_i values suggest that any hydrothermal fluid contribution to the lake from rifting or extensive weathering of rift-related basalts would have been negligible, as Os_i values closer to ~0.13 (Allegre et al., 1999; Miesel et al., 2001) would otherwise be expected. Hence there is no evidence to support a particularly enhanced influx of Fe due to rifting. Instead, the prevalence of ferruginous water column conditions is consistent with low rates of oxidative pyrite weathering driven by only modest levels of atmospheric oxygen (Canfield and Raiswell, 1999). Although it is not possible to directly determine water column sulfate

concentrations, we note that pyrite sulfur isotope compositions are relatively heavy (8.5 ± 6.3‰) throughout most of the Nonesuch Formation (Fig. 2), while a compilation of pyrite sulfur isotope data for the Nonesuch Formation shows a similar distribution (possibly skewed towards slightly heavier values) to 1.5 - 1.0 Ga marine sediments (Fig. 3). This is entirely consistent with a relatively low sulfate environment (e.g., Canfield and Raiswell, 1999), and further supports efficient trapping of sulfide (and hence high S/C ratios; Fig. DR2) driven by a lack of bioturbation, and deposition from a ferruginous system which was sulfur (rather than reactive Fe) limited (e.g., Raiswell and Canfield, 2012).

The distribution of the Nonesuch Formation sulfur isotope data is very different to that observed for 1.18-1.0 Ga lacustrine sediments from NW Scotland (Fig. 3), with no indication of fractionations of the magnitude that would indicate significant oxidative sulfur cycling through microbial disproportionation. This is likely a consequence of the restriction of oxic conditions to surface waters, and limitation of sulfate reduction to sediment porewaters beneath the ferruginous water column of the Nonesuch basin. Together, this would limit formation of the oxidized sulfur species required for disproportionation (Thamdrup et al., 1993). In addition, the low sulfate concentrations inferred for the Nonesuch basin would limit the maximum expression of sulfur isotope fractionation even if oxidative sulfur cycling and disproportionation reactions were prevalent (Canfield and Raiswell, 1999). This is consistent with multiple ($^{32/33/34}$S) sulfur isotope systematics in marine sediments, which suggest that microbial sulfur disproportionation was prevalent by at least 1.3 Ga (Johnston et al., 2005), but was only manifest in the major ($^{32/34}$S) sulphur isotope record after a later Neoproterozoic rise in atmospheric oxygen led to a significant increase in seawater sulfate concentrations (Canfield and Teske, 1996). Thus, rather than reflecting high sulfate concentrations (Hieshima and Pratt, 1991) potentially attributable to extensive oxygenation of the continents under high atmospheric oxygen, Fe-S-C systematics in the Nonesuch

Formation suggest low sulfate concentrations, ferruginous conditions and only modest atmospheric oxygenation.

In light of this, the sulfur isotope data for the Stoer and Torridon Groups may reflect either an unusually sulfate-rich environment that allowed maximum expression of sulfur isotope fractionations (Parnell et al., 2010), or the preservation of large sulfur isotope fractionations through bacterial sulfate reduction alone (Canfield et al., 2010; Sim et al., 2011). Thus, while it remains possible that sulfur isotope systematics in the Stoer and Torridon Groups may be providing an early record of terrestrial oxygenation; our redox and sulfur isotope data for the Nonesuch Formation suggest that early terrestrial oxygenation was not a pervasive feature of localities that preserve evidence for diverse eukaryotic life. Instead, the redox characteristics display strong similarities to the marine realm (Poulton and Canfield, 2011), implying that in terms of water column and atmospheric oxygenation, terrestrial environmental conditions were likely no more pre-disposed towards eukaryote evolution than shallow marine environments. We suggest that the identification and detailed redox evaluation of other late Mesoproterozoic terrestrial sediments should be a priority in order to more precisely evaluate potential links between the redox evolution of aquatic systems and the rich terrestrial biological record.

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FIGURE CAPTIONS

Figure 1: A. Geological map of the Lake Superior region showing the location of the main Keweenawan Supergroup units. The Nonesuch Formation is part of the Oronto Group situated between continental red-beds of the Copper Harbour Conglomerate and the Freda Sandstone and outcrops on the southern shores of Lake Superior. B. Schematic stratigraphy of the Keweenawan Supergroup, focusing on post-rift sediments. The right hand panel illustrates depth variations for each unit. Locations of the Re-Os (1078 ± 24 Ma; this study) and U-Pb (1087.2 ± 1.6 Ma; Davis and Paces, 1990) ages are labelled. Figures adapted from Elmore et al. (1989) and Ojakangas et al. (2001).

Figure 2: Geochemical profiles for the Nonesuch Formation core samples. For the Fe_{HR}/Fe_T and Fe_{Py}/Fe_{HR} graphs the dashed lines show the fields for oxic or anoxic deposition and ferruginous or euxinic deposition, respectively (Poulton and Canfield, 2011). On the Fe_T/Al graph the dashed line represents average anoxic shale (Lyons and Severmann, 2006). On the Fe_{PRS}/Fe_T graph the dashed lines represent modern (Raiswell and Canfield, 1998) and Phanerozoic (Poulton and Raiswell, 2002) averages. CHC stands for Copper Harbour Conglomerate.

Figure 3: Probability density plot of pyrite sulfur isotope data for the Nonesuch Formation (this study; Imbus et al., 1992), the Torridon and Stoer Groups (Parnell et al., 2010) and 1.5 – 1.0 Ga marine sediments (Canfield and Raiswell, 1999).

[1]GSA Data Repository item 2009xxx, which includes a detailed sampling and methodology section, a detailed Re-Os geochronology results section and results tables, is available online

348 at www.geosociety.org/pubs/ft2009.htm, or on request from editing@geosociety.org or

349 Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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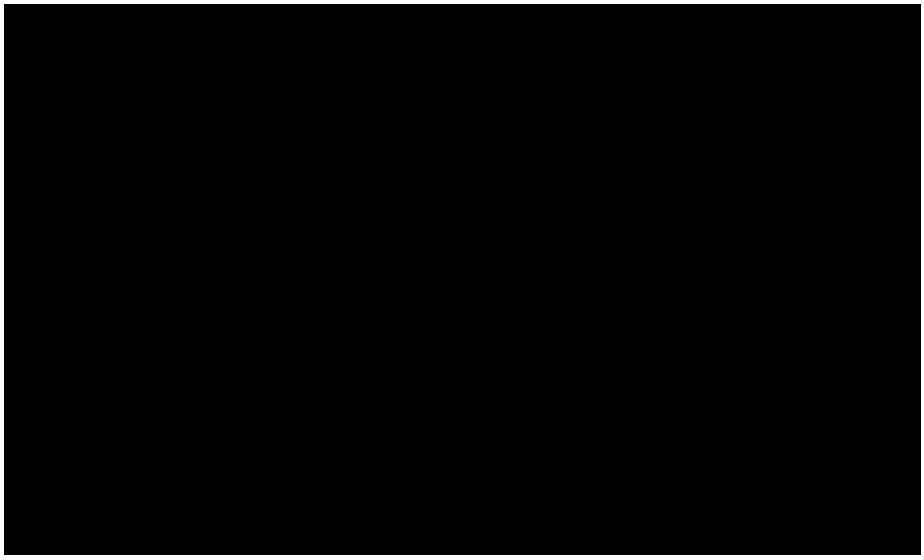
351 **FIGURE 1**



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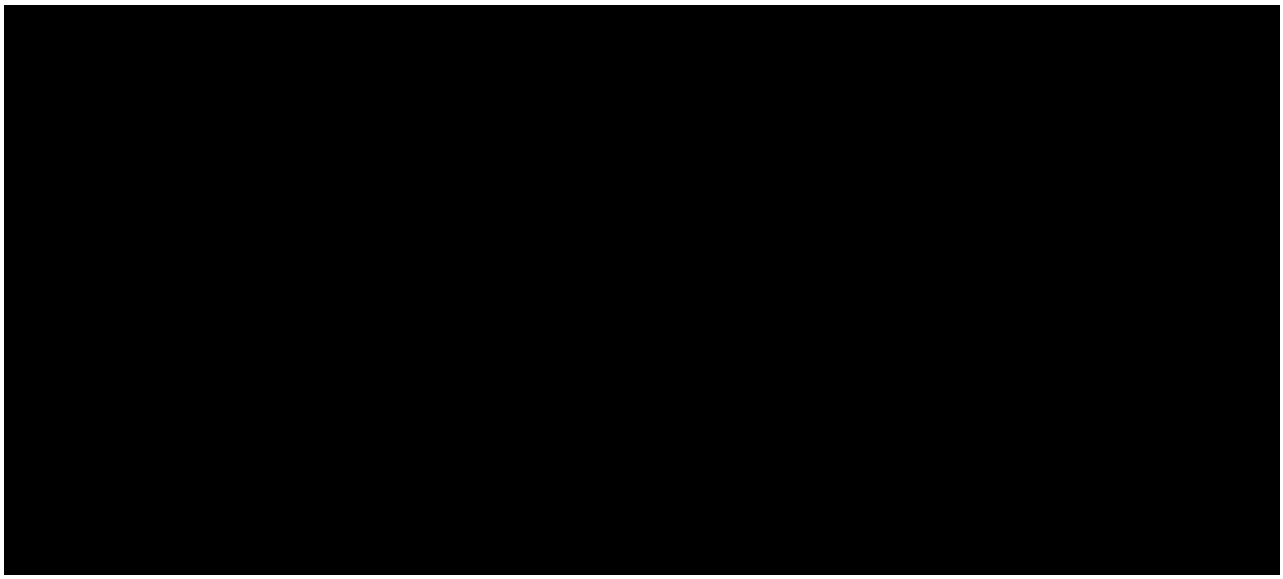
354 **FIGURE 2**

355



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358 **FIGURE 3**